Titration Curves and the Dissociation Constant of Acetic Acid

INSTRUCTOR RESOURCES

The CCLI Initiative

Learning Objectives

The objectives of this experiment are to . . .

- prepare theoretical titration curves for
  - the titration of HCl with NaOH.
  - the titration of $HC_2H_3O_2$ with NaOH. ($HC_2H_3O_2$ is often abbreviated as HOAc)
- perform the experimental titration of $HC_2H_3O_2$ with NaOH using the ***MicroLAB*** Interface.
- analyze the titration data using the ***MicroLAB*** spreadsheet.

Procedure Overview

- the pH of solutions of HCl and $HC_2H_3O_2$ are calculated following addition of various amounts of NaOH. Then a titration curve is constructed using the ***MicroLAB*** Hand Enter data program.
- an acetic acid solution of unknown concentration is titrated with NaOH using the ***MicroLab*** Interface. The molarity of the acetic acid solution is determined.
- a K_a value for acetic acid is calculated at three points along the titration curve.

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TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Report Sheet

Construction of theoretical titration curves

Calculation of HCl with NaOH

ml NaOH	pH	ml NaOH	pH	ml NaOH	pH
0		24.9		30	
2		24.999		32	
5		25		35	
10	1.37	25.001		40	
20		25.1		50	
22		26			
24		28			

Calculations

1. After 0 ml NaOH is added.

2. After 20 ml NaOH is added.

3. After 25 ml NaOH is added.

(4) After 50 ml NaOH is added.

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TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Report Sheet (page 2)

Calculation of $HC_2H_3O_2$ with NaOH

ml NaOH	pH	ml NaOH	pH	ml NaOH	pH
0		24.9		30	
2		24.999		32	
5		25		35	
10	4.57	25.001		40	
20		25.1		50	
22		26			
24		28			

Calculations

1. After 0 ml NaOH is added.

2. After 20 ml NaOH is added.

3. After 25 ml NaOH is added.

4. After 50 ml NaOH is added.

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TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Report Sheet (page 3)

Experimental titration of $HC_2H_3O_2$ with NaOH

Equivalence point volume (ml)		______________________
Molarity of standard NaOH		______________________
Molarity of $HC_2H_3O_2$		______________________
K_a values for $HC_2H_3O_2$	Point 1	______________________
	Point 2	______________________
	Point 3	______________________

Calculations

1. Calculate the molarity of the undiluted acetic acid solution from your data and the concentration of the standard NaOH.

2. Calculate a value for K_a of acetic acid at three points in the buffer region of the curve.

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TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Questions/Problems

1. Describe three ways in which the titration curve of acetic acid (a weak acid) differs from that of hydrochloric acid (a strong acid).

2. Explain why the acetic acid and hydrochloric acid titration curves are identical after the equivalence point.

3. Consider the titration of 50.0 ml of a weak acid, HA, with 0.100 *M* NaOH.

   (a) It requires 43.68 ml of 0.100 *M* NaOH to reach the equivalence point of the titration.

      (1) Calculate the moles of HA present.

      (2) Calculate the original (undiluted) concentration of the weak acid solution.

   (b) During the titration it was observed that after 21.84 ml of 0.100 *M* NaOH had been added the pH of the solution was 6.00. Calculate the K_a for HA.

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Tips and Traps

1. A carbonate free, standardized NaOH solution (~0.1 *M*) is needed. Students can either prepare and standardize the base solution or it can be provided directly.

2. Be sure students record a pH reading before any NaOH is added.

3. Students need not start the titration at a buret reading of 0.00 ml. Have students enter the actual volume reading from the buret when requested.

4. See the file named **Useful Titration Operations** in the **Useful Tools** folder on the CD for information on the following:
   a. Different ways of calibrating the drop counter.
   b. Calibration of the pH probe.
   c. Using the ***MicroLAB*** Drop Counter.
   d. Constructing a formula in the ***MicroLAB*** **Experiment** program.
   e. Slope and Using Derivatives to Determine the Equivalence Point.
   f. Interpolating Between Incremental Values.
   g. Pipetting Technique.
   h. Pipetting Procedure.
   i. Buret Technique.
   j. Performing the Titration.

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Sample Data

Construction of theoretical titration curves
Calculation of HCl with NaOH

ml NaOH	pH	ml NaOH	pH	ml NaOH	pH
0	***1.00***	24.00	***2.69***	26.00	***12.29***
2.00	***1.07***	24.90	***3.70***	28.00	***12.75***
5.00	***1.18***	24.999	***5.70***	30.00	***12.96***
10.00	1.37	25.00	***7.00***	35.00	***13.09***
20.00	***1.95***	25.001	***8.30***	40.00	***13.36***
22.00	***2.19***	25.1	***11.30***	50.00	***13.52***

Calculations

1. After 0 ml NaOH is added.

$$pH = -\log(0.10) = 1.00$$

2. After 20 ml NaOH is added.

$$[H+] = \frac{(0.1\ M)(25\ ml)-(0.1)(20\ ml)}{(25\ ml + 20\ ml)} = \frac{0.5\ mmol}{45\ ml} = 0.011\ M$$

$$[H+] = 0.011\ M \qquad pH = 1.95$$

3. After 25 ml NaOH is added.

$$[H+] = [OH^-] \quad (1 X 10^{-14})\text{\^{}}0.5 = 1 X 10^{-7}, \qquad pH = 7.00$$

4. After 50 ml NaOH is added.

$$[OH-] = \frac{(25\ ml)(0.1\ M)}{(25 + 50)\ ml} = \frac{2.50\ mmol}{75\ ml} = 0.3331\ M \quad pOH = 0.478,$$

$$pH = 14 - 1.64 = 13.52$$

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Sample Data (page 2)

Calculation of $HC_2H_3O_2$ with NaOH

ml NaOH	**pH**	**ml NaOH**	**pH**	**ml NaOH**	**pH**
0	***2.84***	24.00	***6.13***	26.00	***11.29***
2.00	***3.70***	24.90	***7.14***	28.00	***11.75***
5.00	***4.14***	24.999	***8.61***	30.00	***11.96***
10.00	4.57	25.00	***8.70***	35.00	***12.22***
20.00	**5.35**	25.001	***8.81***	40.00	***12.36***
22.00	***5.61***	25.1	***10.30***	50.00	***12.52***

Calculations

1. After 0 ml NaOH is added.

   pH = 2.84

2. After 20 ml NaOH is added.

   pH = 5.35

3. After 25 ml NaOH is added.

   pH = 8.70

4. After 50 ml NaOH is added.

   pH = 12.52

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Sample Data (page 3)

Experimental titration of $HC_2H_3O_2$ with NaOH

Equivalence point volume (ml)		25.05
Molarity of Standard NaOH		0.1118
Molarity of $HC_2H_3O_2$		0.1120
K_a values for $HC_2H_3O_2$	Point 1	1×10^{-5} (7.65 ml NaOH)
	Point 2	1×10^{-5} (13.56 ml NaOH)
	Point 3	1×10^{-5} (19.32 ml NaOH)

Calculations

1. Calculate the molarity of the undiluted acetic acid solution from your data and the concentration of the standard NaOH.

$$\frac{(25.05 \text{ ml } OH^-)(0.1118 \text{ mmol } OH^-)(1 \text{ mmol } H^+)}{(1.00 \text{ ml } OH^-) \quad (1 \text{ mmol } OH^-)} = 0.1120 \text{ M } HC_2H_3O_2$$

2. Calculate a value for K_a of acetic acid at three points in the buffer region of the curve.

at 7.65 ml NaOH, pH = 4.63; $K_a = 1.0 \times 10^{-5}$

$[H^+] = 2.3 \times 10^{-5}$ $[OAc^-] = 7.65 \text{ ml} * 0.1 \text{ M} = 0.024 \text{ M}$

$$[HOAc] = \frac{(0.1 \text{ M ml}*25 - 0.1 \text{ M}*7.65 \text{ ml})}{(25.00+7.65) \text{ ml}} = \frac{2.5-0.77}{32.65 \text{ ml}} = 0.053 \text{ M}$$

$Ka = (2.3 \times 10^{-5})(0.024) / 0.053 = 1.04 \times 10^{-5} = 1.0 \times 10^{-5}$

The following are calculated in similar manner.

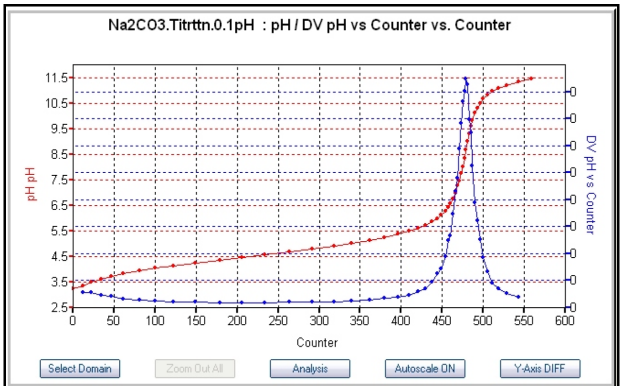
at 13.56 ml NaOH, pH = 5.03; $K_a = 1.1 \times 10^{-5}$

at 19.32 ml NaOH, pH = 5.44; $K_a = 1.2 \times 10^{-5}$

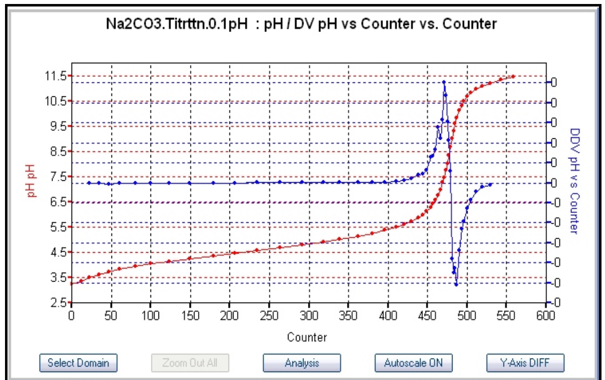
TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Sample Data (page 4)

Sample titration data with first and second derivatives ($HC_2H_3O_2$ with NaOH).



Titration curve for acetic acid (HOAc) with first derivative.



Titration curve for acetic acid (HOAc) with second derivative

A: ml	B: pH	E: DERIV	A: ml	B: pH	E: DERIV
0.00	3.41	0.379	24.91	7.01	2.581
0.60	3.64	0.285	25.00	7.24	9.707
1.18	3.80	0.249	25.05	7.73	29.74
2.01	4.01	0.156	25.10	9.21	11.77
3.25	4.20	0.130	25.15	9.80	4.303
5.02	4.43	0.075	25.21	10.06	2.194
7.65	4.63	0.070	25.29	10.24	1.711
10.61	4.83	0.066	25.45	10.51	0.968
13.56	5.03	0.064	25.69	10.74	0.575
16.80	5.24	0.082	26.04	10.94	0.599
19.32	5.44	0.106	26.29	11.09	0.278
21.30	5.65	0.157	26.94	11.27	0.161
22.80	5.89	0.241	28.21	11.48	0.102
23.70	6.10	0.413	30.21	11.68	0.056
24.30	6.35	0.766	34.10	11.90	0.030
24.61	6.59	1.229	41.31	12.11	0
24.82	6.85	1.778			

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Suggested Answers to Questions/Problems

1. Describe three ways in which the titration curve of acetic acid (a weak acid) differs from that of hydrochloric acid (a strong acid).

   (1) For acetic acid the pH is higher at the beginning, (2) does not rise as steeply during the equivalence point, and the equivalence point occurs at a higher pH for acetic acid.

2. Explain why the acetic acid and hydrochloric acid titration curves are identical after the equivalence point.

   Both depend on the concentration of excess hydroxide ion.

3. Consider the titration of 50.0 ml of a weak acid, HA, with 0.100 *M* NaOH.

   (a) It requires 43.68 ml of 0.100 *M* NaOH to reach the equivalence point of the titration.

   (1) Calculate the moles of HA present.

   $\boldsymbol{4.37 \times 10^{-3}}$ ***mole***

   (2) Calculate the original (undiluted) concentration of the weak acid solution.

   0.0874 M HA

   (b) During the titration it was observed that after 21.84 ml of 0.100 *M* NaOH had been added the pH of the solution was 6.00. Calculate the K_a for HA.

   $$\frac{(21.84 \text{ ml NaOH})(0.100 \text{ mmol NaOH})(1 \text{ mmol OAc}^-)}{(1.00 \text{ ml NaOH})(1 \text{ mmol NaOH})} = 2.184 \text{ mmol OAc}^-$$

   4.37mol HOAc − 2.18 mmol OAc− = 2.19 mmol HOAc remaining

   [HOAc] = [OAc−] therefor $pK_a = pH$, $K_a = 10^{-6} = 1.0 \times 10^{-6}$

TITRATION CURVES AND THE DISSOCIATION CONSTANT OF ACETIC ACID

Laboratory Preparation (per student station)

Equipment

- pH electrode
- ring stand
- buret clamp
- stir bar
- magnetic stirrer
- 50 ml buret
- 25 ml pipet
- 250 ml beaker
- 100 ml graduated cylinder

Chemicals

Actual quantities needed are given below. A 50% excess is recommended.
buffer solutions pH 4, 7, and 10
50 ml standardized NaOH solution (~0.1 *M*)
35 ml unknown acetic acid (~ 0.1 *M*).

Safety and Disposal

- both the acid unknown and NaOH solutions are corrosive. Make sure students wear goggles at all times.
- all resulting solutions may be flushed down the drain with plenty of water.